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⑤④ Stabilized monomer compositions.

⑤⑦ A process for stabilizing an ethylenically unsaturated monomer or oligomer from premature polymerization is disclosed whereby a stabilizing amount of an amine, preferably a substituted hindered amine, in combination with phenothiazine or other related heterocyclic moiety is added to said polymerizable monomer or oligomer. The ethylenically unsaturated monomer or oligomer encompass vinyl monomers or oligomers bearing at least one polymerizable moiety. The combination of substituted hindered amine plus phenothiazine inhibits premature polymerization in the liquid and/or vapor phase.

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S is 1-methoxy-2,2,6,6-tetramethylpiperidin-4-one.

T is 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one.

U is 4-hydroxyethoxy-2,2,6,6-tetramethylpiperidine.

V is bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

W is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

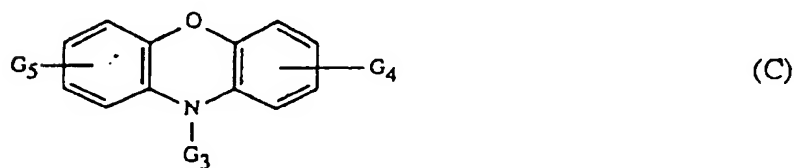
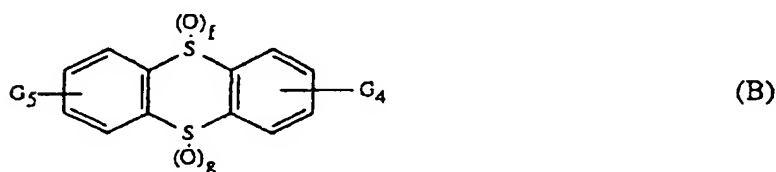
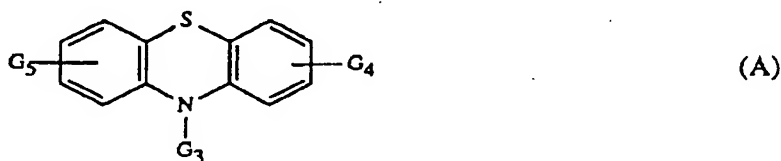
Examples 25-27:

When using the procedure of Example 2, the acrylic acid is replaced respectively with the monomers shown below, no polymer is formed in the presence of 100 ppm of 1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate and 1000 ppm of phenothiazine.

Example	Monomer
25	methyl methacrylate
26	2-hydroxyethyl methacrylate
27	2-hydroxyethyl acrylate

Claims

1. A monomer composition, stabilized against premature polymerization, which comprises
 - (a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and
 - (b) an effective amount, sufficient to inhibit the premature polymerization of component (a), which is a combination of
 - (i) a heterocyclic compound selected from any of formulas A to C



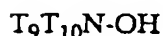
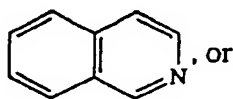
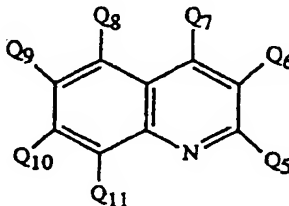
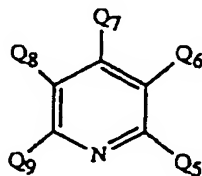
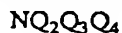
where

G₃ is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms,

G₄ and G₅ are independently hydrogen or alkyl of 1 to 8 carbon atoms, and

f and g are independently 0, 1 or 2, and

(ii) a primary, secondary or tertiary amine, or hydroxylamine, or mixture thereof, of the formula



wherein

Q₂, Q₃ and Q₄ are independently hydrogen, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxy, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 12 carbon atoms or by phenyl, with the proviso that all of Q₂, Q₃ and Q₄ are not hydrogen, cycloalkyl, phenylalkyl or aryl at the same time; or

Q₃ and Q₄ together are straight or branched alkylene of 4 to 8 carbon atoms, 3-oxapentamethylene, 3-thiapentamethylene, 3-iminopentamethylene or 3-methyliminopentamethylene, and Q₂ is hydrogen or alkyl of 1 to 8 carbon atoms;

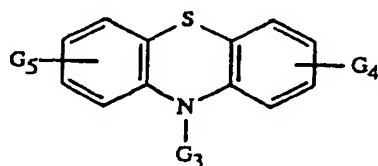
Q₅, Q₆, Q₇, Q₈, Q₉, Q₁₀ and Q₁₁ are independently hydrogen, methyl or ethyl; or

T₉ is hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms, and

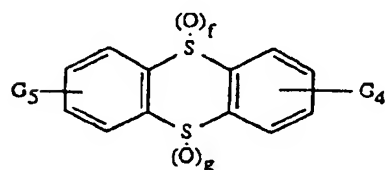
T₁₀ is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or phenylalkyl of 7 to 15 carbon atoms.

2. A composition according to claim 1 wherein the effective amount is a combination of component (i) and component (ii) in a weight ratio of (i):(ii) of 1:10 to 1000:1, preferably 1:1 to 10:1, and where the total concentration of (i) plus (ii) is in the range of 50-10,000 ppm, preferably 200-600 ppm, based on the monomer being stabilized.
3. A composition according to claim 1 wherein component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.

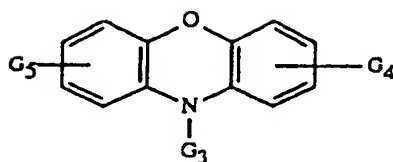
4. A composition according to claim 4 wherein the monomer is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate, preferably styrene, butadiene, acrylic acid or methacrylic acid.
5. A composition according to claim 1 wherein component (i) is phenothiazine.
6. A composition according to claim 1 wherein component (ii) is N,N-diethylhydroxylamine or N,N-di-tert-butylhydroxylamine.
7. A composition according to claim 1 which additionally contains another stabilizer selected from the group consisting of hydroquinone and monomethyl ether of hydroquinone.
8. A process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises
 adding to said monomer (a) an effective amount of a combination of compounds of component (b) according to claim 1.
9. A process according to claim 8 for preventing the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a monomer polymerizable by free radical initiation which comprises
 adding to said monomer (a), before processing is begun, an effective amount of a combination of compounds of component (b) according to claim 1.
10. A process according to claim 8 which comprises
 adding 50 to 10,000 ppm of component (b), according to claim 1, in a weight ratio of from 1:10 to 1000:1, to a continuous feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, of any ethylenically unsaturated monomer present in the feed stream, and
 further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.
11. A monomer composition, stabilized against premature polymerization, which comprises
 (a) an ethylenically unsaturated monomer or mixture of monomers, polymerizable by free radical initiation, and
 (b) an effective amount, sufficient to inhibit premature polymerization of component (a), of a combination of
 (i) a heterocyclic compound selected from any of formulas A to D



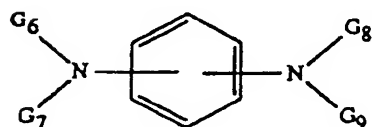
(A)



(B)



(C)



(D)

where

G_3 is hydrogen, alkyl of 1 to 4 carbon atoms or alkenyl of 3 to 4 carbon atoms,

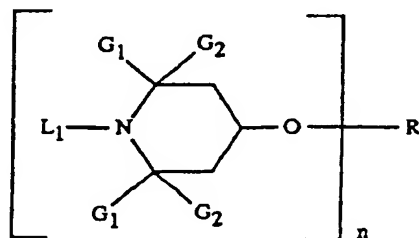
G_4 and G_5 are independently hydrogen or alkyl of 1 to 8 carbon atoms,

G_6 is aryl of 6 to 10 carbon atoms or aralkyl of 7 to 15 carbon atoms, and

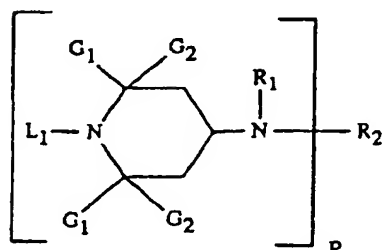
G_7 , G_8 and G_9 are independently hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms or alkaryl of 7 to 15 carbon atoms;

f and g are independently 0, 1 or 2, and

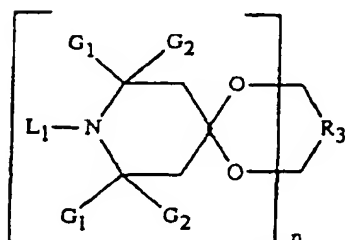
(ii) a compound or mixture of compounds of any of formulas I to XIX



(I)



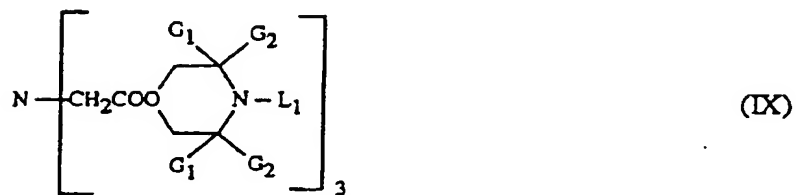
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(III)



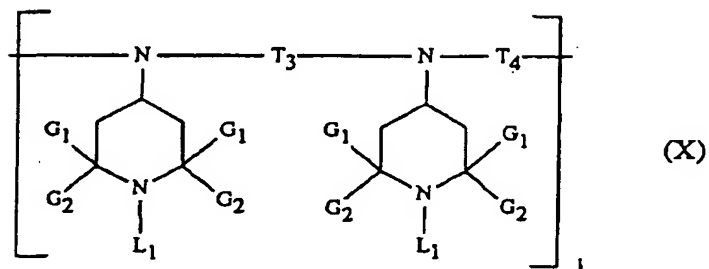
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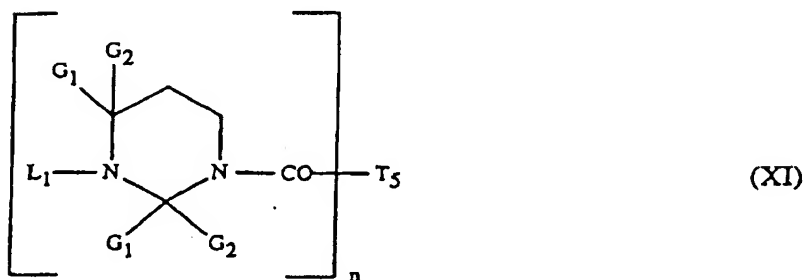
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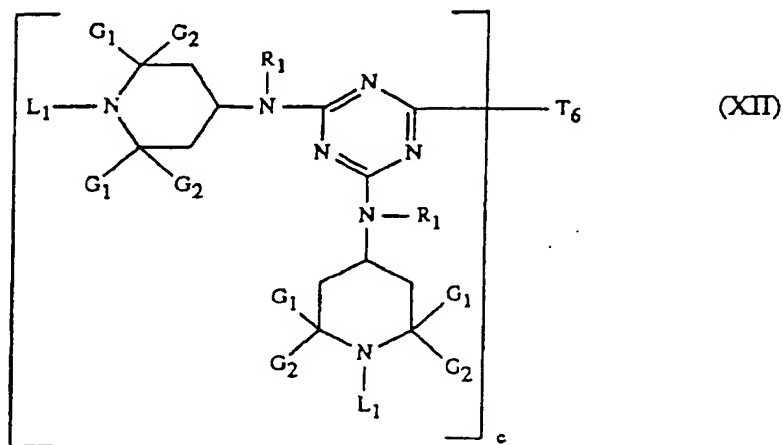
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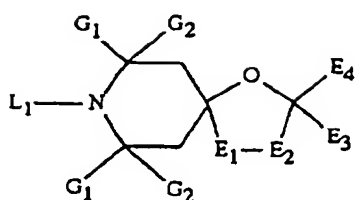
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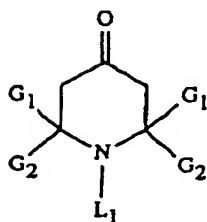
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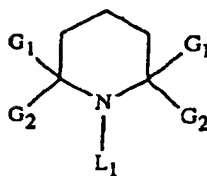
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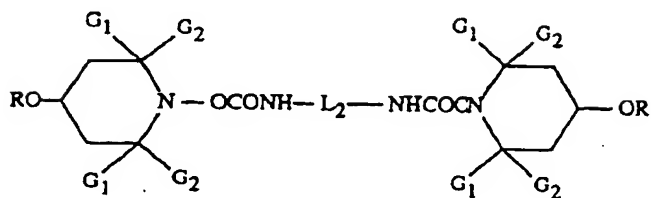
(XIII)



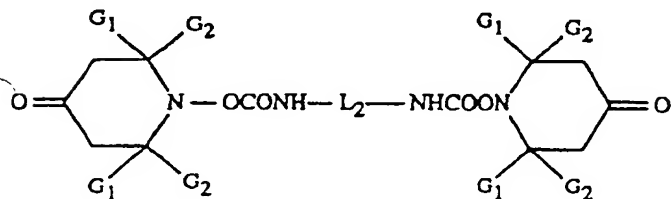
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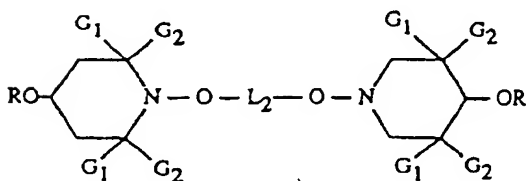
(XV)



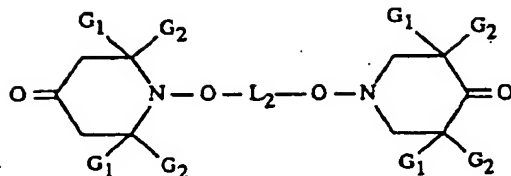
XVI



XVII



XVIII



XIX

wherein

G_1 and G_2 are independently alkyl of 1 to 4 carbon atoms;

L_1 is hydrogen, hydroxyl, alkyl of 1 to 18 carbon atoms, said alkyl substituted by hydroxyl, cyanoethyl, glycidyl, aralkyl of 7 to 15 carbon atoms or a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, $-OCONHL_3$ or $-OL_4$, where

L_3 is hydrogen, alkyl of 2 to 18 carbon atoms, allyl, cyclohexyl, aryl of 6 to 10 carbon atoms, said aryl substituted by one or two alkyl groups of 1 to 4 carbon atoms or is benzyl,

L_4 is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, alkenyl of 2 to 18 carbon atoms, cycloalkenyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, a radical of a saturated or unsaturated bicyclic or tricyclic hydrocarbon of 7 to 12 carbon atoms or aryl of 6 to 10 carbon atoms or said aryl substituted by alkyl of 1 to 4 carbon atoms, or L_4 is $-CH_2CH_2COOL_5$ where L_5 is alkyl of 1 to 18 carbon atoms, n is 1 or 2,

when n is 1,

R is hydrogen, C_1 - C_{18} -alkyl optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic acid, or of carbamic acid or of a phosphorus-containing acid, or a monovalent silyl radical; or

when n is 2,

R is C_1 - C_{12} -alkylene, C_4 - C_{12} -alkenylene, xylylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, or of a dicarbamic acid or of a phosphorus-containing acid, or a bivalent silyl radical;

p is 1, 2 or 3,

R_1 is C_1 - C_{12} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_8 -aralkyl, C_2 - C_{18} -alkanoyl, C_3 - C_5 -alkenoyl or benzoyl;

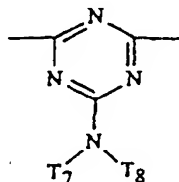
when p is 1,

R_2 is C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_2 - C_8 -alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula $-CONH-Z$ wherein Z is hydrogen, methyl or phenyl; or

when p is 2,

R_2 is C_2 - C_{12} -alkylene, C_8 - C_{12} -arylene, xylylene, a $-CH_2CH(OH)CH_2-O-X-O-CH_2CH(OH)CH_2-$ wherein X is C_2 - C_{10} -alkylene, C_8 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene; or, provided that R_1 is not alkanoyl, alkenoyl or benzoyl, R_2 can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group $-CO-$; or R_1 and R_2 together when p is 1 can be the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid; or

R_2 is



where T_7 and T_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T_7 and T_8 together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene;

when p is 3,

R_2 is 2,4,6-triazinyl;

when n is 1,

R_3 is C_2 - C_8 -alkylene or hydroxyalkylene or C_4 - C_{22} -acyloxyalkylene; or

when n is 2,

R_3 is $(-CH_2)_2C(CH_2)_2$;

when n is 1,

R_4 is hydrogen, C_1 - C_{12} -alkyl, C_3 - C_5 -alkenyl, C_7 - C_9 -aralkyl, C_5 - C_7 -cycloalkyl, C_2 - C_6 -alkoxyalkyl, C_6 - C_{10} -aryl, glycidyl, a group of formula $-(CH_2)_m-COO-Q$ or of the formula $-(CH_2)_m-O-CO-Q$ wherein m is 1 or 2 and Q is C_1 - C_4 -alkyl or phenyl; or

when n is 2,

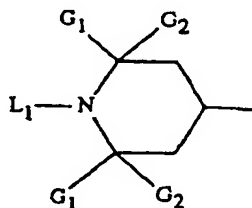
R_4 is C_2 - C_{12} -alkylene, C_6 - C_{12} -arylene, a group $-CH_2CH(OH)CH_2-O-X-O-CH_2CH(OH)CH_2-$ wherein X is C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene, or a group $-CH_2CH(OZ_1)CH_2-(OCH_2CH(OZ_1)CH_2)_2-$ wherein Z_1 is hydrogen, C_1 - C_{18} -alkyl, allyl, benzyl, C_2 - C_{12} -alkanoyl or benzoyl;

R_5 is hydrogen, C_1 - C_{12} -alkyl, allyl, benzyl, glycidyl or C_2 - C_6 -alkoxyalkyl;

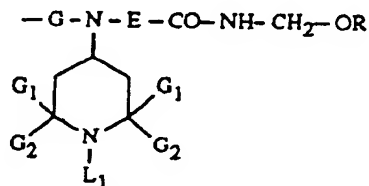
Q_1 is $-N(R_7)-$ or $-O-$;

E is C_1 - C_3 -alkylene, the group $-CH_2CH(R_8)-O-$ wherein R_8 is hydrogen, methyl or phenyl, the group $-(CH_2)_3-NH-$ or a direct bond;

R_7 is C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_{12} -aralkyl, cyanoethyl, C_6 - C_{10} -aryl, the group $-CH_2CH(R_8)-OH$; or a group of the formula



or a group of the formula



wherein G is C_2 - C_6 -alkylene or C_6 - C_{12} -arylene; or

R_7 is a group $-E-CO-NH-CH_2-OR_8$;

R_8 is hydrogen or C_1 - C_{18} -alkyl;

Formula VI denotes a recurring structural unit of a polymer where T is ethylene or 1,2-propylene, or is a repeating structural unit derived from an α -olefin copolymer with an alkyl acrylate or methacrylate;

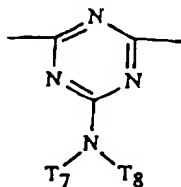
k is 2 to 100;

T_1 has the same meaning as R_2 when p is 1 or 2;

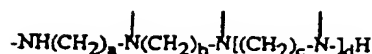
M and Y are independently methylene or carbonyl;

T_2 has the same meaning as R_4 , and T_2 is octamethylene;

T_3 and T_4 are independently alkylene of 2 to 12 carbon atoms, of T_4 is



T_5 is



where a, b and c are independently 2 or 3, and d is 0 or 1;

e is 3 or 4;

T_5 is the same as R with the proviso that T_5 cannot be hydrogen when n is 1;

E_1 and E_2 , being different, are each oxo or imino;

E_3 is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms; and

E_4 is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms; or E_3 and E_4 together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by up to four alkyl groups of 1 to 4 carbon atoms;

L_2 is a divalent radical from an aliphatic, cycloaliphatic or aromatic diisocyanate from which the two -NCO groups are removed, or is an alkanediyl of 1 to 18 carbon atoms or cyclohexanediyl

12. A composition according to claim 11 wherein the effective amount is a combination of component (i) and component (ii) in a weight ratio of (i):(ii) of 1:10 to 1000:1, preferably 1:1 to 10:1, and where the total concentration of (i) plus (ii) is in the range of 50-10,000 ppm, preferably 200-600 ppm, preferably 200-600 ppm, based on the monomer being stabilized.

13. A composition according to claim 11 wherein component (a) is a monomer selected from the group consisting of the olefinic hydrocarbons, dienes, halogenated monomers, unsaturated acids, unsaturated esters, unsaturated amides, unsaturated nitriles, unsaturated ethers, acrylated urethanes and unsaturated polyesters and mixtures thereof.

14. A composition according to claim 13 wherein the monomer is styrene, butadiene, vinyl chloride, acrylic acid, methacrylic acid, vinyl acetate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, trimethylolpropane triacrylate, polyethylene glycol diacrylate or methyl methacrylate, preferably styrene, butadiene, acrylic acid or methacrylic acid.

15. A composition according to claim 11 wherein component (i) is phenothiazine.

16. A composition according to claim 11 wherein component (ii) is of formula I or XV, preferably of formula I.

17. A composition according to claim 11 wherein component (ii) is selected from the group consisting of 1-[2-(methoxycarbonyl)ethoxy]-4-benzyloxy-2,2,6,6-tetramethyl piperidine;

1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;

bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yl] phthalate;

1-tert-butoxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;

4-hydroxy-1-octyloxy-2,2,6,6-tetramethylpiperidine;

1-[2-(methoxycarbonyl)ethoxy]-2,2,6,6-tetramethylpiperidine;

1-methylcyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;

4-benzyloxy-1-ethoxy-2,2,6,6-tetramethylpiperidine;

1-carbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine;

4-hydroxy-1,2,2,6,6-pentamethylpiperidine;

1-butylcarbamoyloxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine;

1- α -methylbenzyloxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate;

1,4-dimethoxy-2,2,6,6-tetramethylpiperidine;

bis[1-(2-(methoxycarbonyl)ethoxy)-2,2,6,6-tetramethylpiperidin-4-yloxy]-p-xylylene;

1-hydroxy-2,2,6,6-piperidin-4-yl benzoate;

4-hydroxy-1-methoxy-2,2,6,6-tetramethylpiperidine;

1-methoxy-2,2,6,6-tetramethylpiperidin-4-one;

1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one;

4-hydroxyethoxy-2,2,6,6-tetramethylpiperidine;
bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate; and
bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

- 5 18. A composition according to claim 11 which additionally contains another stabilizer selected from the group consisting of hydroquinone and monomethyl ether of hydroquinone.
19. A process for preventing the premature polymerization of a monomer polymerizable by free radical initiation which comprises
- 10 adding to said monomer (a) an effective amount of a combination of compounds of component (b) according to claim 11.
20. A process according to claim 19 for preventing the fouling of processing equipment including reactors, pipes, stills, distillation columns, cracking towers and heat transfer surfaces during the processing of a
- 15 monomer polymerizable by free radical initiation which comprises adding to said monomer, before processing is begun, an effective amount of a combination of compounds of component (b) according to claim 11.
21. A process according to claim 19 which comprises
- 20 adding 50 to 10,000 ppm of a mixture of components (i) and (ii), according to claim 13, in a weight ratio of from 1:10 to 1000:1, to a continuous feed stream to deactivate the autocatalytic polymerization, in any part of the continuous process equipment, of any ethylenically unsaturated monomer present in the feed stream, and
- 25 further adding to said feed stream an additional 10 ppm to 500 ppm of said mixture as a makeup additive to maintain the desired concentration of said mixture in the fluid feed stream being processed.
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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91810561.0

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>US - A - 4 912 247</u> (P.V. ROLING) * Claims * --	1-5, 7, 11-15, 18	C 07 C 69/54 C 07 C 57/075 C 07 C 15/46 C 07 C 67/62 C 07 C 7/20
D,A	<u>US - A - 4 668 721</u> (R. SELTZER et al.) * Column 3, line 45 - column 13, line 53; claims * --	11-13	
D,A	<u>US - A - 4 691 015</u> (R.A. BEHRENS et al.) * Column 1, line 45 - column 10, line 29; claims * --	11-13, 18	
A	<u>EP - A1 - 0 334 500</u> (UNIROYAL) * Claims * ----	1-5, 11-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 07 C 7/00 C 07 C 15/00 C 07 C 51/00 C 07 C 57/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 07-10-1991	Examiner HOFBAUER
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